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FACTORS AFFECTING STABILITY AND EQUILIBRIA OF FREE RADICALS

STERIC FACTORS IN HYDRAZYLS

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Abstract—The preparation of 1,1-diphenyl-2-(2,4- and 2,6-dinitrophenylhydrazine) is described. Lead peroxide converts them into hydrazyl free radicals, but only the latter may be isolated in crystalline form. Ultra-violet and visible absorption spectra of hydrazines and hydrazyls are compared.

Factors Affecting the Stability of Equilibrium Free Radicals

IT is today well established that the stability of triarylmethyl free radicals is due both to *conjugative* and to *steric factors*.[1,2] Changes in dissociation of *para*-substituted hexa-arylethanes are usually attributed to the former factors, while the latter are reflected in the large effects of *ortho*-substituents on the same dissociation.

The *conjugative factors* were the first to be explored, and it was found that both electron-repelling and electron-attracting substituents enhance the dissociation of hexa-arylethanes.[1b,2b] In the nitrogen series, Wieland observed[3] that electron-repelling substituents (Me_2N, MeO, Me) increase the dissociation of tetra-arylhydrazines while electron-attracting groups (Br,NO_2) exert the opposite effect. This difference between carbon and nitrogen radicals was tentatively explained[4] and confirmed by newer measurements on the dissociation of 1,1,4,4,-tetra-aryl-2,3-benzoyltetrazanes.[5]

The steric factors may be further subdivided into two antagonistic steric effects. The *direct steric effect*[*] is exerted on the central bond in the dimer (hexa-arylethane, tetra-arylhydrazine, diarylperoxide); owing to steric repulsion this bond is lengthened and weakened, favouring the dissociation. The *indirects teric effect*[*] is exerted on the aryl groups in the radical: steric repulsions causes them to be twisted, the radical

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[*] In order to carry the subsequent discussion we had to find names for these two steric effects: the first is purely steric, the second is exerted through reduction of conjugation, therefore the names "direct-indirect" were adopted.

[1] [a] W. A. Waters, *The Chemistry of Free Radicals.* Butterworths, London (1948); [b] J. E. Leffler, *The Reactive Intermediates of Organic Chemistry* Chapters 1 and 4. Interscience, New York (1956); [c] C. Walling, *Free Radicals in Solution* pp. 162, 524, 530. John Wiley, New York (1957); [d] D. J. E. Ingram, *Free Radicals as Studied by Electron Spin Resonance* p. 138. Butterworths, London (1958); [e] D. H. Hey, *Ann. Rep.* **37**, 250 (1940).

[2] [a] A. E. Remick, *Electronic Interpretations of Organic Chemistry* (2nd Ed) p. 326. John Wiley, New York (1949); [b] M. J. S. Dewar, *The Electronic Theory of Organic Chemistry* Chap. 12. Clarendon Press, Oxford (1950); [c] G. W. Wheland, *Resonance in Organic Chemistry* pp. 382–393. John Wiley, New York (1955); [d] J. Hine, *Physical Organic Chemistry* Chap. 18. McGraw-Hill, New York (1956); [e] O. A. Reutov, *Theoreticheskie problemy organicheskoi khimil* (Edited by Moscow Univ.) Chap. 5 (1956); [f] G. E. K. Branch and M. Calvin, *The Theory of Organic Chemistry* p. 326. Prentice-Hall, New York (1941).

[3] H. Wieland, *Die Hydrazine* p. 71. F. Enke Verlag Stuttgart (1913); *Liebigs Ann.* **381**, 200 (1911); *Ber. Dtsch. Chem. Ges.* **48**, 1078 (1915); H. Wieland and A. Wecker, *Ibid.* **55**, 1804 (1922), and further references therein.

[4] H. Burton and C. K. Ingold, *Proc. Leeds Phil. Soc.* **1**, 430 (1929); G. N. Lewis and D. Lipkin, *J. Amer. Chem. Soc.* **63**, 3232 (1941); M. J. S. Dewar, *Ibid.* **74**, 3353 (1952).

[5] N. Schwartz and W. K. Willmarth, *J. Chem. Phys.* **20**, 748 (1952); W. K. Willmarth and N. Schwartz, *J. Amer. Chem. Soc.* **77**, 4543, 4551 (1955).

assumes a non-planar form ("propeller" for triarylmethyls) which reduces the conjugation in the radical and thus the dissociation is reduced. These steric effects can hardly be separated, but the former usually predominates over the latter, the net result being that bulky *ortho*-alkyl groups tremendously stabilize triarylmethyl and even diarylmethyl radicals[6] (the effect is largely steric since *o*-methoxy groups do not show it[7]). Only in some bridged compounds with fixed steric configuration can these two effects be separated, e.g. the tripticyl radical is instable[8] because only the indirect steric effect is at work (for a stable triphenylmethyl radical with rigid oxygen bridges *cf.*[9]) In the case of oxygen free radicals, bulky t-butyl[10] or phenyl[11] groups in both *ortho* positions are essential for the stability of aroxyls; here only the direct steric effect is involved.

Nitrogen free radicals differ from carbon free radicals in that they do not react with oxygen. Indeed, this is one of the reasons why 1,1-diphenyl-2-picryl-hydrazyl[12] (2,4,6-yl*: I, $R = R' = H$) is so widely used as a standard free radical for electron spin resonance measurements.[1d,13] The other reason is its stability: it has no tendency towards dimerization in solution or in crystalline state even at low temepratures[14] and it does not disproportionate even on prolonged heating. The unreactivity of 2,4,6-yl extends even to the reaction with the characteristic reagent for nitrogen radicals, NO. On the other hand 2,4,6-yl readily gives hydrogen abstractions[15] and other redox reactions[16] and reacts with stable[12] or transient[17] carbon free radicals; these are its

[*] This shorthand notation will be preferred over the usual one, DPPH, because it may be applied to hydrazines and hydrazyls differently substituted with nitro-groups.

[6] J. B. Conant and M. Bigelos, *J. Amer. Chem. Soc.* **50**, 2041 (1928); W. T. Nauta, P. J. Wuir and D. Mulder, *Chem. Weekbl.* **37**, 96 (1940) and further references therein; C. S. Marvel, J. S. Kaplan and C. M. Himmel, *J. Amer. Chem. Soc.* **63**, 1892 (1941) and previous papers; K. Ziegler, *Liebigs Ann.* **551**, 127 (1942); W. Theilacker, H, Schulz, U. Baumgarte, H. G. Drössler, W. Rohde, F. Thater and H. Uffmann, *Angew. Chem.* **69**, 322 (1957).

[7] S. T. Bowden, *J. Chem. Soc.* 4257 (1957) and previous papers.

[8] P. D. Bartlett, M. J. Ryan and S. G. Cohen, *J. Amer. Chem. Soc.* **64**, 2649 (1942); E. C. Kooyman and A. Strang, *Rec. Trav. Chim.* **72**, 329 (1953); U. Schöllkopf, *Angew. Chem.* **72**, 147 (1960).

[9] O. Neunhoffer and H. Haase, *Chem. Ber.* **91**, 1801 (1958).

[10] C. D. Cook, C. B. Depatie and E. S. English, *J. Org. Chem.* **24**, 1356 (1959) and previous papers in the series; E. Müller, *Neure Anschauungen der organischen Chemie* (2nd Ed.) p. 392. Springer Verlag, Berlin (1957); E. Müller and K. Ley, *Chem. Ber.* **92**, 2278 (1959) and previous papers in the series; J. C. McGowan and T. Powell, *J. Chem. Soc.* 238 (1960); A. Rieche, B. Elschner and M. Landbeck, *Angew. Chem.* **72**, 385 (1960).

[11] K. Dimroth, F. Kalk and G. Neubauer, *Chem. Ber.* **90**, 2058 (1957); K. Dimroth, F. Kalk, R. Sell and K. Schlömer, *Liebigs Ann.* **624**, 51 (1959).

[12] S. Goldschmidt and K. Benn, *Ber. Dtsch. Chem. Ges.* **55**, 628 (1922).

[13] J. J. Lothe and G. Eia, *Acta Chem. Scand.* **12**, 1535 (1958); G. Berthet, *Ann. Phys.* **3**, 629 (1958).

[14] H. J. Gerritsen, R. Okkes, H. M. Gijsman and J. van den Handel, *Physica* **20**, 13 (1954); S. L. Singer and C. Kikuchi, *J. Chem. Phys.* **23**, 1738 (1955).

[15] E. A. Braude, A. G. Brook and R. P. Linstead, *J. Chem. Soc.* 3574 (1954); K. E. Russell, *J. Phys. Chem.* **58**, 437 (1954); D. Mauzcrall and F. H. Westheimer, *J. Amer. Chem. Soc.* **77**, 2261 (1955); H. Watanabe and K. Kido, *J. Chem. Soc. Japan Ind. Chem. Sect.* **60**, 1476 (1957); J. E. Hazell and K. E. Russell *Canad. J. Chem.* **36**, 1729 (1958); A. G. Brook, R. J. Anderson and J. T. Van Patot, *Ibid.* 159; A. H. Ewald, *Trans. Faraday Soc.* **55**, 792 (1959); A. A. Balandin, M. L. Khidekel and V. V. Patrikeev, *Izv. Akad. Nauk SSSR, Otdel. Khim. Nauk* 361 (1959).

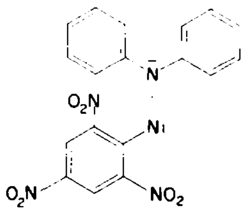
[16] L. H. Sutcliffe and J. Walkley *Nature, Lond.* **178**, 999 (1956).

[17] P. D. Barlett and H. Kwart, *J. Amer. Chem. Soc.* **72**, 1051 (1960); C. E. H. Bawn and R. G. Halford, *Trans. Faraday Soc.* **51**, 780 (1955); C. E. H. Bawn and D. Verdin, *Ibid.* **56**, 519 (1960); M. Pike and F. Watson, *J. Polymer Sci.* **9**, 229 (1952); A. Henglein, *Makromol. Chem.* **15**, 188 (1955); **20**, 83 (1956); M. Calvin and J. A. Barltrop, *J. Amer. Chem. Soc.* **74**, 6513 (1952); H. P. Kaufmann and L. Korfhage, *Fette u. Seifen* **55**, 281 (1953); K. E. Russell and A. V. Tobolsky, *J. Amer. Chem. Soc.* **75**, 5052 (1953); **76**, 395 (1954); G. M. Burnett and W. W. Wright, *Proc. Roy. Soc.* A **221**, 41 (1954); A. S. Kuzminski and L. A. Angert, *Dokl. Akad. Nauk SSSR* **96**, 1187 (1954); J. L. Kice, *J. Amer. Chem. Soc.* **76**, 6274 (1954); G. S. Hammond, J. N. Sen and C. E. Boozer, *J. Amer. Chem. Soc.* **77**, 3244 (1955) and previous papers; G. A. Razuvaev and V. N. Latyaeva, *Zh. Obschhei Khim.* **26**, 1986 (1956); A. F. Bickel and E. C. Kooyman, *J. Chem. Soc.* 2217, 2415 (1957); J. C. McGowan and T. Powell, *J. Appl. Chem.* **9**, 93 (1959); *J. Chem. Soc.* 3103 (1959); C. H. Bamford and A. D. Jenkins, *Proc. Roy. Soc.* A **228**, 220 (1955).

two main chemical applications (oxidizing action in redox systems, and radical scavenging and counting; for limitations in the latter reaction see[18] and for chemical dosimetry of ionising radiations see[19]).

2,4,6-Yl is exceptional among other nitrogen[3] or hydrazyl[20] free radicals, not only because of its amazing stability, but, and especially, because of the contradictory effect of nitro groups, which in 2,4,6-yl contrary to all other nitrogen free radicals, exert a stabilizing influence. This "puzzling"[1b] contradiction disappears if one postulates that the stability of 2,4,6-yl is not electronically, but sterically conditioned. Until now no consistent discussion of the steric effects on the stability of nitrogen free radicals has been published, though for carbon and oxygen free radicals the importance of the steric factor has clearly been recognized.[1,2] Only an indirect steric effect has been mentioned[21] in the case of tetra-arylhydrazines. We suppose on the contrary, that in 2,4,6-yl a stabilizing direct steric effect is operating.

The studies of free radicals related with 2,4,6-yl did not bear on the sterical but on the electronic effects: related radicals were prepared, modifying the diarylamino moiety through various substituents R and R′ in I.[22-25] Even in the two somewhat



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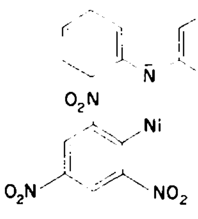

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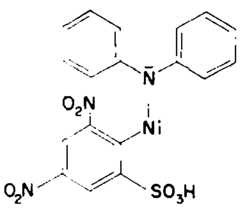
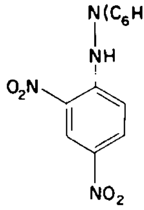


III

differently related radicals II[26,27] and III,[26] the steric relationships are practically unaltered.

We therefore investigated hydrazyl free radicals with modified steric environments.



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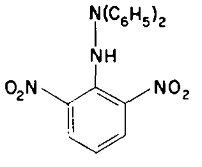

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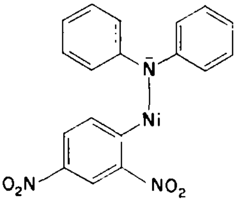

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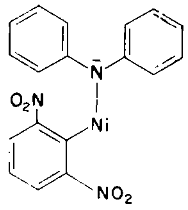

VII

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[18] J. C. Bevington, *Nature, Lond.* **175**, 477 (1955); *J. Chem. Soc.* 1127 (1956); W. I. Bengough, *Chem. & Ind.* 599 (1955); H. Morawetz, *Formation and Trapping of Free Radicals* (Edited by A. M. Bass and H. P. Broida) pp. 363, 374. Academic Press, New York (1960).

[19] L. Bouby and A. Chapiro, *J. Chim. Phys.* **54**, 341 (1957) and previous papers.

[20] S. Goldschmidt, *Ber. Dtsch. Chem. Ges.* **53**, 44 (1920); *Liebigs Ann.* **437**, 194 (1924); V. Franzen, *Ibid.* **604**, 251 (1957); F. Benington, E. V. Shoop and R. H. Poirier, *J. Org. Chem.* **18**, 1506 (1953).

[21] L. B. Radina, Z. V. Pushkareva and Z. Iu. Kokoshko, *Dokl. Akad. Nauk SSSR* **123**, 483 (1958); cf. also Z. V. Pushkareva and L. B. Radina, *Ibid.* 301.

[22] R. H. Poirier and F. Benington, *J. Org. Chem.* **19**, 1157 (1954).

[23] R. I. Walter, R. S. Codrington, A. F. D'Adamo Jr. and H. C. Torrey, *J. Chem. Phys.* **25**, 319 (1956).

[24] R. O. Matevosian, I. Ia. Postovski and A. K. Tchirkov, *Zh. Obshchei Khim.* **29**, 858 (1959).

[25] R. G. Bennett and A. Henglein, *J. Chem. Phys.* **30**, 1117 (1959).

[26] H. S. Jarrett, *J. Chem. Phys.* **21**, 761 (1953).

[27] C. Kikuchi and V. W. Cohen, *Phys. Rev.* **85**, 379 (1952); **93**, 394 (1954).

The present paper describes the synthesis and properties of radicals VI and VII in which the picryl group in 2,4,6-yl has been replaced by a 2,6- or 2,4-dinitrophenyl group.

RESULTS AND DISCUSSION

The general method of Goldschmidt and Renn[12] was followed, namely the nucleophilic aromatic substitution through 1,1-diphenyl-hydrazine of a halogen atom activated by *o*- and *p*-nitro groups, to yield the triarylhydrazines IV and V respectively, which were subsequently dehydrogenated with lead peroxide (PbO_2). While 2,6-dinitrochlorobenzene reacted normally, though much less readily than picryl chloride, it was not possible to prepare 2,4-ine (IV) starting from 2,4-dinitrochlorobenzene which yielded only solvolysis products. However, 2,4-ine was readily prepared with the much more reactive 2,4-dinitrofluorobenzene, which reacted with 1,1-diphenylhydrazine almost as rapidly as picryl chloride. On the other hand, 1,1-diphenylhydrazine did not substitute *p*-nitrofluorobenzene even under drastic conditions (had this reaction been successful, a third radical with both *ortho* positions free from steric interference would have been prepared).

The oxidation with lead peroxide proceeded normally, yielding in both cases violet solutions (in chloroform, 1,2-dichloroethane or benzene), very similar with the 2,4,6-yl solutions. The radical 2,6-yl (VII) was easily isolated through evaporation of the solvent and recrystallization from benzene–ligroin.

However, the radical 2,4-yl (VI) could not be isolated in crystalline state, because its solutions became brown on concentration (even at low temperature and in the absence of air), and its benzenic solution prepared in the cold deposited only a brown product on dilution with petroleum ether. This brown product gave no paramagnetic resonance absorption and consequently was no longer a radical. In dilute solution, 2,4-yl is stable for several days.

This difference between 2,4-yl and 2,6-yl strikingly illustrates the importance of steric effects for the stability of triarylhydrazyl free radicals: while in both 2,4-yl and 2,6-yl the electronic effects are comparable, only 2,6-yl with both *o*-positions occupied by bulky nitro-groups is stable and monomeric in crystalline state; with one *o*-position free, 2,4-yl is appreciably less sterically hindered than 2,4,6-yl or 2,6-yl and that explains why it is not able to be isolated in solid state; whether the brown compound is formed from it through dimerization, disproportionation, or other reaction such as intramolecular substitution to a phenazone derivative cannot be definitely ascertained as yet. Though it is not safe to draw conclusions from unsuccessful experiments, we believe that the failure to isolate 2,4-yl in solid state is significant, and that it proves that 2,4-yl is less stable than 2,6-yl.

Absorption spectra

Ultra-violet and visible absorption spectra were determined for the three hydrazines 2,4,6-ine, 2,4-ine (IV) and 2,6-ine (V) in neutral and alkaline methanol solutions, and for the three radicals 2,4,6-yl, 2,4-yl and 2,6-yl in 1,2-dichloroethane solution. The absorption spectra are given in Figs. 1–3, and through graphical interpolation the bands shown in Table 1 were found. The results for 2,4,6-yl and 2,4,6-ine are in agreement with reported spectra[28],[29] (no data below 260 mμ were previously given).

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[28] S. Goldschimdt and F. Graef, *Ber. Dtsch. Chem. Ges.* **61**, 1858 (1928).

[29] R. H. Poirier, E. J. Kahler and F. Benington, *J. Org. Chem.* **17**, 1437 (1953).

The relevant features are summarized in the following items:

1. All three hydrazines have three bands in neutral solution, at ca. 225, 265 and 330 mμ (the last band is shifted with 60 mμ towards the visible and its intensity is decreased in 2,6-ine). The total Σf value is remarkably constant (1·1). for all three hydrazines.

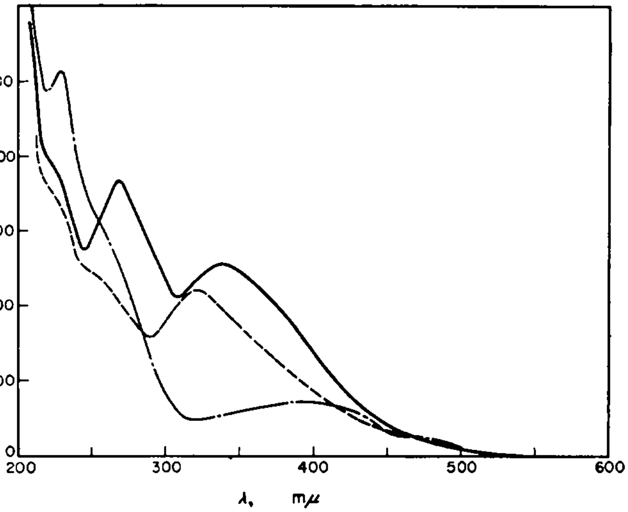

Fig. 1. Absorption spectra of 2,4-ine (full line), 2,6-ine (dashed-dotted line) and 2,4,6-ine (dashed line) in methanol.

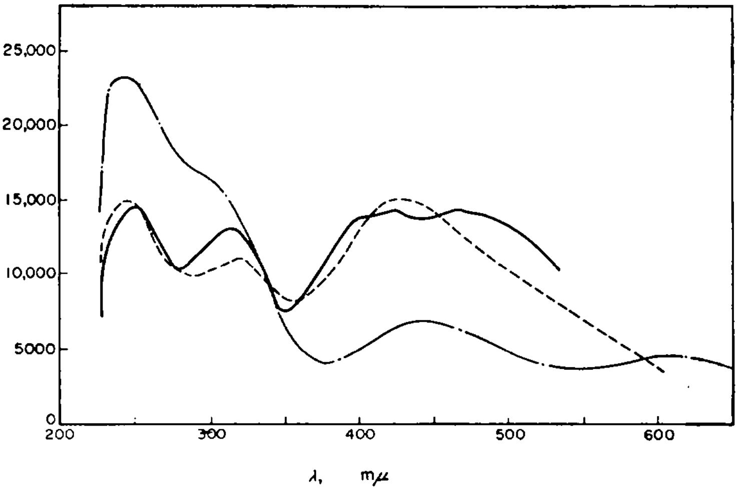

Fig. 2. Absorption spectra of 2,4-ine (full line), 2,6-ine (dashed-dotted line) and 2,4,6-ine (dashed line) in 90% methanol with 0·5 N sodium hydroxide.

2. In basic solution the situation is less clear-cut: 0·05 N NaOH solutions considerably affect the colour of 2,4,6-ine, yielding a spectrum essentially identical with that of 0·5 N NaOH solutions; however, 2,4-ine and even more 2,6-ine do not change colour in 0·05 N NaOH solutions and the absorption spectra do not differ from spectra determined in neutral solution. The greater acidity of 2,4,6-ine is not surprising, since

it has one activating nitro group more. In 0·5 N NaOH solution, 2,4-ine becomes violet-brown like 2,4,6-ine, and 2,6-ine becomes green. The spectrum of 2,4,6-ine presents three bands at ca. 250, 320 and 430 mμ; the last band is split into two closely situated bands in 2,4-ine (ca. 400 and 430 mμ: interpolation errors were rather high in this case owing to the shape of the band envelope) and into two distanced bands in 2,6-ine (440 and 610 mμ). As in the previous case, the longest wave length band in 2,6-ine has a considerable lower frequency and intensity than in the other two hydrazines, and the three Σ*f* values are fairly constant (1·5). The shape of the spectrum for 2,4,6-ine in basic medium suggests the possible presence of a small band completely masked, at about 290 mμ with ε ca. 4500.

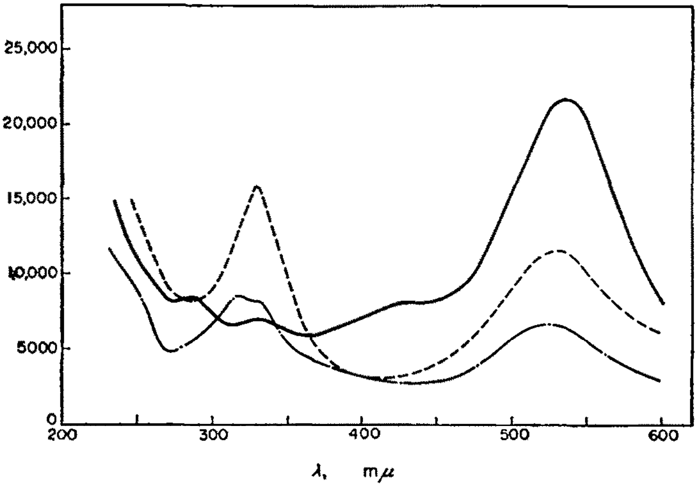

Fig. 3. Absorption spectra of 2,4-yl (full line), 2,6-yl (dashed–dotted line) and 2,4,6-yl (dashed line) in 1,2-dichloroethane.

3. All three free radicals present a band at 530 mμ, responsible for the violet colour, though its wave length and intensity in 2,6-yl are smaller than in the other two radicals (this is the reason that solutions of 2,6-yl have nearly the same nuance but are more pale than solutions in equal concentrations of the other two radicals), and another band at 330 mμ. However, the remainder of the spectrum is quite different: 2,4,6-yl contains no more bands; 2,6-yl has a band at 315 mμ and possibly a completely masked band with λ_{max} 375 mμ, ε_{max} 2800, *f* 0·048, whose presence is suggested by the asymmetry of the descending branches of the 330 mμ band; and 2,4-yl contains two distinct bands at 288 and 435 mμ. The last spectrum was determined immediately after oxidation with PbO_2 of a solution of 2,4-ine in dichloroethane; the possibility is however not excluded that in this case the decomposition products of the radical manifest themselves in the absorption spectrum: the 435 mμ band could possibly originate in this way, and if this were true the sensibly higher Σ*f* value for 2,4-yl would come into line with the other two radicals (0·5).

Previous spectra of 2,4,6-yl were determined in chloroform [28,29](cf. also[22,30]). Using 1,2-dichloroethane we advanced about 30 mμ into the ultra-violet range. In order to enlarge still further the spectral range, the spectra of 2,6-yl and 2,4,6-yl were also determined in di-n-butyl ether (the solubility is satisfactory) and in cyclohexane

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[30] R. H. Poirier and F. Benington, *J. Org. Chem.* **19**, 1847 (1954).

TABLE 1. ABSORPTION BANDS OF 1,1-DIPHENYL-2-POLYNITROPHENYL-HYDRAZINES AND -HYDRAZYLS[a]

Compound and solvent	2,4-Dinitro						2,6-Dinitro						2,4,6-Trinitro					
	Apparent[b]		Interpolated[c]				Apparent		Interpolated				Apparent		Interpolated			
	λ	ε	λ	ε	f	Σf	λ	ε	λ	ε	f	Σf	λ	ε	λ	ε	f	Σf
Hydrazine Methanol	225*s*	19000	231	12000	0·195	1·17	230	25800	230	25000	0·47	1·02	215*s*	17700	222	17000	0·51	1·18
	267	18800	267	14000	0·37		260*s*	15000	260	13000	0·40		260*s*	11800	257	7500	0·163	
	338	12800	338	12800	0·61		394	3700	394	3700	0·151		322	11000	322	11000	0·51	
Hydrazine (sodium salt) 0·5 N NaOH in 90% methanol	250	14800	250	14500	0·62	1·65	245	23000	242	23000	0·95	1·62	244	15200	244	15000	0·62	1·40
	310	13000	310	13000	0·40		300*s*	16000	305	16000	0·42		320	11100	320	8000	0·125	
	425	14200	395	13000	0·41		440	6800	440	6800	0·153		431	15100	431	15100	0·65	
	465	14300	490	13500	0·22		610	4400	610	4400	0·101							
Hydrazyl	288	8400	286	6300	0·132	0·91	315	8400	313	7500	0·16	0·49						0·59
	330	7000	332	7000	0·25		330*s*	8300	332	7000	0·20		332	15800	332	15800	0·37	
	435[d]	8000	436	7500	0·16													
1,2-Dichloroethane	537	21700	536	21700	0·37		513	6700	513	6700	0·13		530	11700	530	11700	0·22	

[a] Wavelengths in mμ; spectral limits were 210 mμ for methanol and 240 mμ for dichloroethane.

[b] A shoulder (inflexion) is denoted by *s*.

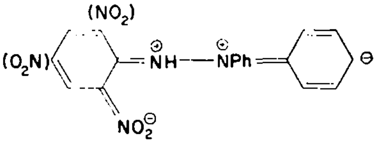
[c] The interpolation was done graphically; in view of the considerable uncertainties in some interpolated data for λ_{max} and ε_{max}, f values were not calculated through integration, but through the approximate formula $f = 4{\cdot}32 \cdot 10^{-9} \cdot \varepsilon_{max} \cdot \Delta\nu_{max\frac{1}{2}}$. Completely masked bands for basic 2,4,6-ine and 2,6-yl, apparent only in the interpolation procedure, are not separately shown (see text).

[d] This band is possibly due to decomposition products of the radical (see text and experimental part).

(very small solubility). An extremely intense band at the spectral limit (205 mμ) was apparent for both radicals with a slight inflexion at 237 mμ. Small hipso- and hypochromic effects were noted in the solvent sequence dichloroethane → dibutyl ether → cyclohexane.

The assignment of electronic transitions can be done, tentatively and qualitatively, for all bands excepting those with shortest wave lengths.

The band with longest wave length in the hydrazine spectrum (neutral solution) is due to the partial chromophore[31,32] comprising the polynitrophenyl group and the adjacent NH group. A conjugation throughout the molecule would cause absorption at wave lengths greater than 400 mμ. Such a conjugation is impossible both for electronic (because it would imply highly improbable structures like VIII with adjacent positive nitrogen atoms) and for steric reasons. Molecular models after Stewart-Briegleb show that diphenylamine is non-planar; in the arrangement nearest to



VIII

coplanarity the two phenyl rings make a dihedral angle of ca. 150° (this is the largest possible dihedral angle). In 1,1-diphenylhydrazine the same situation occurs, but it is apparent that the two hydrogens bonded to nitrogen are not equivalent: one of them is completely screened by the hydrogen atoms in *ortho*-positions. This N-bonded hydrogen is to be found also in triarylhydrazines, namely IV and V, since it cannot be replaced by other groups. The polynitroaryl group is perpendicular to the approximate plane of the two phenyl groups. Nitro groups in *ortho* positions have no space for free rotation and they are twisted out from conjugation with the aromatic ring. The situation must parallel the configuration of picryl iodide, where X-ray diffraction studies showed[33] that *ortho*-nitro groups were twisted and had large C—N distances, while the *para*-nitro group was coplanar and had a small C—N distance (an X-ray diffraction study of 2,4,6-ine, 2,4,6-yl and related substances would be highly interesting, not only because it would clear up the problem of steric configurations, but also because it would show how solvent molecules are complexed in radical crystals[34–36]).

While the lack of conjugation through two hydrazinic nitrogen atoms has been agreed upon,[37] it seems that even in diphenylamine derivatives and related substances, a conjugative effect is absent,[32] although previous reports reported the contrary.[37,38]

The second band in the spectra of hydrazines, at ca. 265 mμ, can possibly be due to the other partial chromophore, the diphenylamino moiety. The hipsochromic shift from the corresponding band in diphenylamine (285 mμ) could be ascribed to

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[31] P. Grammaticakis, *Bull. Soc. Chim. Fr.* **99**, 1372 (1954) and previous papers.

[32] V. A. Izmail'ski and K. A. Nuridjanian, *Dokl. Akad. Nauk SSSR* **129**, 1053 (1959); **133**, 594 (1960).

[33] G. Hase and H. M. Powell, *J. Chem. Soc.* 1398 (1940).

[34] M. Sternberg, *C. R. Acad. Sci., Paris* **240**, 990 (1955).

[35] J. A. Lyons and W. F. Watson, *J. Polymer Sci.* **18**, 141 (1955).

[36] A. E. Arbuzov, F. G. Valitova, N. S. Garif'ianov and B. M. Kozyrev, *Dokl. Akad. Nauk SSSR* **126**, 774 (1959).

[37] F. Bohlmann, *Chem. Ber.* **84**, 490 (1951).

[38] H. H. Jaffé, *J. Chem. Phys.* **22**, 1430 (1954).

steric factors. (*Cf.* recent illustrations of absorption due to partial chromophores in tetraphenyls[39] and in pyrylium salts[40]).

In hydrazyl free radicals and in hydrazine anions, both electronic and steric factors are changed: electronically, structures like VIII with two positive adjacent nitrogens are no more involved; sterically, the configuration has changed owing to modified hydradization in the radical, and to disparition of the N—H . . . O—N hydrogen bond.[29,30] Thus, conjugation throughout the molecule is allowed, giving rise to the 530 mμ band in the radical and to absorption beyond 400 mμ in hydrazine anions.

The smaller number of bands in 2,4,6-yl and 2,4,6-ine anion indicates a higher degree of symmetry, as in the well-known case of malachite green and crystal violet. The splitting of the longer wave length band of 2,6-ine in basic medium (like 2,4-ine) and the exceptional bathochromic and hypochromic effects observed for the longer wave length bands in 2,6-ine in neutral and basic medium, can be accounted for by admitting that in 2,6-ine the two nitro groups are not equivalent, as formula V would suggest.

The band at 300–330 mμ in hydrazyls and hydrazine anions can analogously be ascribed to electronic transitions involving a semi-resp. fully-occupied orbital in the diphenylamino moiety.

Infra-red and ESR spectra will be reported later.

EXPERIMENTAL

It was claimed[41] that the preparation of 1,1-diphenylhydrazine was critical for the yield and the quality of 2,4,6-yl. Since our results are somewhat different, we are describing the preparation of 1,1-diphenylhydrazine, 2,4,6-ine and 2,4,6-yl.

Preparation of 1,1-*diphenylhydrazine.* Diphenylnitrosamine[42,43] (40 g, 0·2 moles), m.p. 66–67° (from ligroin) in 200 ml ethanol with 64 g (1 mole) high-grade zinc powder, was gradually treated with external cooling with 80 ml glacial acetic acid. The temp rising suddenly (30–40°), was kept between 20–25° by cooling and addition rate. The mixture was stirred for 1–2 hr longer until a sample failed to develop a blue colour on dilution with conc HCl. The white zinc complex was filtered off, then washed with ethanol (air moisture causes heating, and occasionally zinc acetate crystallizes in the filtrate), and the filtrate was treated with 2 l. HCl *d* 1·19. 1,1-Diphenylhydrazine hydrochloride was filtered off on sintered glass filter, washed with conc HCl and dried in a dessiccator (90–95% yield). The recrystallization[41] from HCl was accompanied by considerable losses and was unnecessary if the reduction has been carried out cautiously. If in the reduction anhydrous ethanol and acetic acid are used, the reaction proceeds less rapidly and less exothermally, the zinc powder does not become white and does not become warm on filtration, but the yield is substantially the same, an anhydrous medium is therefore unnecessary. By alkalinization, ether extraction and distillation under reduced pressure[41,45] 1,1-diphenylhydrazine is obtained as a colourless liquid with b.p. 165°/5 mm, b.p. 172°/8 mm, in 70–80% yield.

Preparation of 1,1-*diphenyl-2-picryl-hydrazine and -hydrazyl.* Picryl chloride was prepared from pyridine picrate with phosphorus oxychloride[45]* (which cannot be replaced by thionyl chloride). Equivalent amounts (20 mmoles) of diphenylhydrazine (3·7 g), picryl chloride (5·0 g) and sodium bicarbonate (1·7 g) in hot ethanol[39] yielded in 30 min the orange-red 2,4,6-ine (7·8 g, 99%), which may

* Compare.[46]

[39] R. H. Wiley and B. J. Wakefield, *J. Org. Chem.* **25**, 132 (1960).

[40] A. T. Balaban, V. E. Sahini and E. Keplinger, *Tetrahedron* **9**, 163 (1960); A. T. Balaban and C. D. Nenitzescu, *Izv. Akad. Nauk SSSR., Otdel khim. Nauk* 2064 (1960).

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[44] H. Wieland and E. Müller, *Ber. Dtsch. Chem. Ges.* **46**, 3308 (1913).

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[46] K. Okón, *Rocz. Chem.* **33**, 45 (1959).

be recrystallized from benzene–ethanol or chloroform–ethanol, m.p. 174–175°. The conversion into 2,4,6-yl was effected by shaking for 2 hr with the equal amount of anhydrous sodium sulphate and a 20-times larger amount of lead peroxide in chloroform or benzene, and diluting after filtration with ether or ligroin. The radical crystallizes with solvent molecules which are lost by cautious heating under vacuum, and which caused the differences initially observed in the m.p. (*cf.*[34–36] and the last reference from[16]) and were responsible for variations in data concerning radical scavenging and ESR measurements.[36]

Preparation of 1,1-*diphenyl*-2-(2,4-*dinitrophenyl*)-*hydrazine*. 2,4-Dinitrofluorobenzene[47] (7 g, 37·5 mmoles) was refluxed for 1 hr with 7 g (37·5 mmoles) 1,1-diphenylhydrazine and 5·5 g (75 mmoles) sodium bicarbonate in 150 ml ethanol. Then 70 ml chloroform was added for solubilization of 2,4-ine and the solution was filtered and concentrated under reduced press. After cooling, filtering and washing with a small amount of ethanol, 12·5 g crude product m.p. 118° were obtained. Recrystallization from 450 ml ethanol afforded orange-red needles m.p. 120°, 10·5 g (Found: C, 61·8; H, 4·2; N, 16·1. $C_{18}H_{14}N_4O_4$ requires: C, 61·7; H, 4·0; N, 16·0%).

In the oxidation with lead peroxide in chloroform as described for 2,4,6-yl, a deep violet colour develops, and the solution affords an ESR signal, but attempts to isolate the radical in solid state through evaporation of the solvent under reduced press or dilution with ether failed: the solution became brown and deposited a brown material m.p. (dec.) 174° (from benzene–ligroin) which afforded no ESR signal. Its absorption spectrum showed bands at ca. 270, 340 and 440 mμ, with absorption intensities decreasing in this order. (Found: C, 61·05; H, 3·7; N, 14·75%).

Preparation of 1,1-*diphenyl*-2-(2,6-*dinitrophenyl*)-*hydrazine and -hydrazyl*. 2,6-Dinitrochlorobenzene[48] m.p. 78° (4·0 g, 20 mmoles) and 7·2 g (40 mmoles), diphenylhydrazine were refluxed for 40 hr in 150 ml ethanol. The brown-coloured product was filtered off, and purified through repeated recrystallizations from ethanol. On scratching, the orange-coloured 2,6-ine crystallized first, then a coffee-brown oxidation product, separated by rapid filtration. A better purification is achieved by chromatographic separation on alumina from benzene, 2,6-ine being eluted first, (5·5 g, 78%, m.p. 142–143°, deep orange (Found: C, 61·9; H, 4·0; N, 16·1. $C_{18}H_{14}N_4O_4$ requires: C, 61·7; H, 4·0; N, 16·0%), followed by the coffee-brown oxidation product. This crystallizes from ethanol in glistening leaflets m.p. 128° and yields orange-coloured solutions in 1,2-dichloroethane, whose absorption spectrum is nearly identical with the spectrum of 2,6-ine in neutral or basic medium (only the 400 mμ maximum is shifted with 10 mμ towards longer wavelengths). (Found: C, 60·8; H, 4·1; N, 14·9%). Its treatment with lead peroxide in dichloroethane affords a pink solution with absorption maxima at 254, 313 and 510 mμ.

Oxidation of 2,6-ine with lead peroxide in chloroform in the presence of sodium sulphate as described for 2,4,6-yl affords 2,6-yl in 95% yield. Recristallization from benzene–ligroin gives black-violet leaflets m.p. dec. 167°. Solutions in benzene, chloroform or dichloroethane are violet; only at very low concentrations ($2\cdot10^{-8}$ molar) can these solutions be discerned from 2,4,6-yl solutions of the same concentration (the latter are somewhat redder and were intensely coloured). (Found: C, 61·5; H, 3·7; N, 15·6; $C_{18}H_{13}N_4O_4$ requires: C, 61·9; H, 3·75; N, 16·0%).

Ultra-violet and visible absorption spectra were recorded at room temp with a Zeiss spectrophotometer.

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